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Preparation of sulphuryl fluoride

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(56) Related Art

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Abstract

Sulphuryl fluoride can be prepared selectively in a high yield from sulphur dioxide and elemental fluorine in the presence of an alkali fluoride and hydrogen fluoride. The preferred alkali fluoride is potassium fluoride.

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Invention Title: PREPARATION OF SULPHURYL FLUORIDE

The following statement is a full description of this invention, including the best method of performing it known to us :-

Preparation of sulphuryl fluoride

The invention relates to a process for the preparation of sulphuryl fluoride.

Sulphuryl fluoride is used, for example, as a fumigant for insecticidal purposes. It is already known that sulphuryl fluoride can be prepared from sulphur dioxide and fluorine in the gas phase, see H. Moissan and P. Lebeau in Ann. Chim. Phys. [7] 26 (1902), pages 145 to 178, in particular pages 159 to 169. However, this type of preparation is very risky, since explosions may occur.

It was an object of the present invention to devise a process with which sulphuryl fluoride can be prepared in a high yield and with high purity. This object is achieved by the process according to the invention.

The process according to the invention provides for sulphur dioxide and elemental fluorine to be reacted together in the presence of an alkali fluoride and hydrogen fluoride. In this case, the hydrogen fluoride is present in the liquid phase. Preferably the alkali fluoride is present in the form of a solution in hydrogen fluoride. For example, the alkali fluoride may be used dissolved in HF. However, it may also be added as a solid to HF, and for example also as a precursor (e.g. as carbonate). It then dissolves during the reaction until it is dissolved in the HF.

"Alkali fluoride" stands for LiF, NaF, KF, CsF and RbF, preferably KF. Of course, the alkali fluoride may also be used as an HF adduct.

The fluorine may be used in pure form or as a mixture with inert gas (e.g. N_2, Ar, etc.).

Expediently, one operates in the temperature range from -60 to +50°C, preferably -10°C to +20°C. The pressure is preferably in the range from ambient pressure (about 1 bar absolute) to 10 bar (absolute).

The molar ratio of SO_2 to F_2 is expediently in the range from 0.9:1 to 1.1:1. The alkali fluoride is preferably present dissolved in the reaction mixture in a quantity of 1 to 20% by weight. The hydrogen fluoride may be used in a stoichiometric excess; it functions as a solvent for the alkali fluoride.

For working-up, it is possible, for example, to condense out excess HF from the reaction mixture which is removed in gaseous form. The reaction mixture which has not condensed out is then washed, e.g. with water containing hydrogen peroxide. The remaining pure SO_2F_2 is then dried, compressed and poured into steel flasks.

The process according to the invention may, for example, be performed as a batch reaction. Alternatively, it is also possible to operate continuously, for example by circulating part of the reaction mixture and isolating resulting sulphuryl fluoride therefrom (as described under "working-up"). Hydrogen fluoride which condenses out is recycled.

The process according to the invention has the advantage that it is very selective - hardly any secondary reactions take place. The reaction takes place rapidly and completely, and at low temperatures.

The following examples are intended to explain the invention further, without restricting its scope.

Example 1:

Preparation of sulphuryl fluoride / two-stage addition of fluorine

$$SO_2 + F_2 \text{ --------> } SO_2F_2$$

Batch:

HF	64	g
KF	10	g (0.17 mole)
SO_2	11	g (0.17 mole)
F_2	3.8	l (0.17 mole)

Performance:

KF was placed in a 300 ml autoclave, and HF was metered in with ice cooling. Thereupon, strong evolution of heat was observed, and the temperature in the autoclave rose from 2°C to 24°C.

After cooling to 0°C, the addition of SO_2 took place. No evolution of heat could be detected. Then F_2 was metered in up to a pressure of 6 bar (corresponding to one-half of the stoichiometric quantity). Then the reaction mixture was brought to 21°C (pressure 6 bar).

In an oil bath, the reaction mixture was heated to 40°C. No pressure increase was recorded. Then the reaction mixture was cooled with dry ice (at -59°C, the pressure was approximately 2 bar), and F_2 was again fed in up to a pressure of 7 bar. The cold bath was removed, and at 23°C the pressure in the autoclave was 7 bar. The contents of the autoclave were again heated to 40°C (no increase in pressure). Then they were cooled to -76°C. The pressure was then 1 bar.

The pressure in the autoclave was brought to 5 bar with N_2 10 times and purged.

At 22°C, the pressure was 5 bar. The reaction gas was passed through KI solution. Since no discolouration was observed, no F_2 was contained in the reaction gas.

The reaction mixture was investigated using gas chromatography (GC/MS).

Result:

Total Area 1294930

RetTime	Area	Area %	Name
3.19	561350	43.383	Air
3.31	15766	1.219	SF_6
3.42	48575	3.754	CO_2
3.51	644997	49.848	SO_2F_2
3.75	8716	0.674	SOF_2
3.91	2265	0.175	--
4.05	91	0.007	--
4.76	9267	0.716	SO_2
10.74	1837	0.142	CFC-113
13.58	1066	0.082	--

Example 2:

Preparation of sulphuryl fluoride / single-stage addition of fluorine

Batch:

HF	50 g
KF	5 g (0.08 mole)
SO_2	6 g (0.09 mole)
F_2	1.9 l (0.09 mole)

Performance:

HF, KF and SO_2 were initially introduced. Once 6 bar F_2 had been metered in, slight evolution of heat observed,

and the temperature of the reaction mixture rose from 2°C to 7°C.

After one hour, the pressure had dropped to 2.5 bar (at 20°C 2.8 bar). A gas sample over dry KI showed no discolouration; this proved that no F_2 was contained in the gas sample.

Then the gas was passed through a washing bottle with aqueous KF solution in the gas collection tube and GC/MS measurements were recorded.

Result:

Total Area 1119065

RetTime	Area	Area %	Name
3.17	653122	58.363	Air
3.29	2603	0.233	SF_6
3.41	3577	0.320	CO_2
3.49	453955	40.566	SO_2F_2
3.74	5770	0.516	--
3.91	38	0.003	--

Example 3:

Preparation of sulphuryl fluoride with LiF

Batch:

HF	55 g
LiF	2.6 g (0.1 mole)
SO_2	10 g (0.1 mole)
F_2	1.9 l (0.1 mole)

Performance:

LiF was placed in the autoclave, and HF, SO_2 and fluorine (7 bar) were added with ice cooling. The

reaction mixture was left to stand overnight, and then was kept for 1 hour at 40°C. The reaction mixture was filled 10 times with 5 bar nitrogen each time and purged. The remaining reaction mixture was investigated by gas chromatography.

Result:

Total Area 1446847

RetTime	Area	Area %	Name
3.17	603814	41.733	Air
3.29	1330	0.092	SF_6
3.41	9602	0.664	CO_2
3.48	809773	55.968	SO_2F_2
3.73	3404	0.235	SOF_2
3.88	11	0.011	--
3.92	7	0.001	--
4.04	412	0.029	--
4.59	16895	1.168	H_2O
4.75	1599	0.111	SO_2

Comparison example:

Preparation of sulphuryl fluoride without alkali fluoride

Reaction:

$$SO_2 + F_2 \text{ --------> } SO_2F_2$$

Batch:

HF	58 g
SO_2	8 g (0.09 mole)
F_2	3 l (0.08 mole)

Performance:

Performance:

HF and SO_2 were placed in the autoclave with ice cooling, and fluorine was added (7 bar). The reaction mixture was left to stand overnight and then, once it had been passed through aqueous KF, was investigated by gas chromatography. The gas chromatography demonstrated a high content of SOF_2.

Result:

Total Area 1058218

RetTime	Area	Area %	Name
3.17	631714	59.696	Air
3.29	1165	0.110	SF_6
3.41	3243	0.307	CO_2
3.50	391816	37.026	SO_2F_2
3.74	29889	2.824	SOF_2
4.75	92	0.009	SO_2
6.88	299	0.028	--

Claims

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the preparation of sulphuryl fluoride, wherein sulphur dioxide and elemental fluorine are reacted in the presence of an alkali fluoride and liquid hydrogen fluoride to form sulphuryl fluoride.

2. A process according to Claim 1, characterised in that the alkali fluoride is used dissolved in hydrogen fluoride.

3. A process according to Claim 1 or 2, characterised in that the process is operated at a temperature in the range from -60 to +50°C.

4. A process according to any one of the preceding claims, characterised in that the alkali fluoride, hydrogen fluoride and sulphur dioxide are initially introduced and elemental fluorine is introduced into the mixture.

5. A process according to any one of the preceding claims, characterised in that potassium fluoride is used as the alkali fluoride.

6. A process according to any one of the preceding claims, characterised in that the process is performed continuously, with part of the reaction mixture being recirculated.

DATED this 10th day of November 1999.

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